



32 343. WO.0

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08J 5/18, B32B 27/08	A1	(11) International Publication Number: WO 93/06159	(43) International Publication Date: 1 April 1993 (01.04.93)
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(21) International Application Number: PCT/US92/08064

(22) International Filing Date: 23 September 1992 (23.09.92)

(30) Priority data:
766,690 27 September 1991 (27.09.91) US

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(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).

Published
With international search report.

(54) Title: BARRIER FILM

(57) Abstract

Films featuring improved barrier properties formed essentially from a polychlorotetrafluoroethylene having a number average molecular weight of about 1,000,000, or alternately a ZST of 200, preferably 150 and less. The films are useful in forming multilayer film structures, molded articles and the like which exhibit improved barrier properties to gases and vapors, particularly to water vapors. A process for producing such a film and particular articles formed incorporating the film are also disclosed.

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BARRIER FILM

BACKGROUND

1. Field of the Invention

The present invention relates to thermoplastic
5 films and film forming compositions; more particularly
the present invention relates to film forming
compositions comprising polychlorotrifluoroethylene and
films formed therefrom where such films feature
improved water vapor transmission barrier properties.

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2. Description of the Prior Art

As will certainly be appreciated by those
conversant with the art a wide of thermoplastic resins
are presently known. Articles formed from such
15 thermoplastic resins, i.e., shaped profiles, plates,
sheets, films, complex articles, all which feature
physical and chemical property characteristics which
are directly related to thermoplastic resin from which
they are formed. Films formed from thermoplastic
20 resins feature chemical and physical characteristics
which are directly related to the thermoplastic resin
which they are formed.

Important physical characteristics of films which
are of great interest to the art include the
25 permeability of the film and its consequent resistance
to the transmission of gases, aromas, and/or vapors
such as water vapor. Such properties are especially
important in the film art as films are often utilized
in applications wherein such properties are critical;
30 one example of which includes the use of films as a
packaging material for foodstuffs or medicaments. A
further application is the utilization of such films

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and/or composite films comprising two or more layers of two or more films forming for use in bags, as a wrapping material, or alternately for formed containers. In applications such as those latter described, it is highly desirable to utilize two or more films to form a multilayered film structure which provides structural integrity, low vapor or gas transmission, and good formability.

While there are films presently known to the art provide useful structures, there remains a continuing need in the art for further improvements in films and film structures, particularly those which provide a film structure featuring low water vapor transmission, and good physical characteristics.

15

SUMMARY

According to one aspect of the present invention, there is provided an improved film structure comprising a poly(chlorotrifluoroethylene) (hereinafter sometimes interchangeably referred to as "PCTFE") film which features low water vapor transmission and good physical strength.

In a still further aspect of the present invention, there is provided an improved PCTFE film which provides improved resistance to the transmission of water vapor at film thicknesses previously unavailable to art prior to the present invention.

In a still further aspect of the present invention, there is provided an improved PCTFE film having a thickness up to about 15 mils which features improved water vapor transmission rate properties.

In a further aspect of the present invention, there is provided a film structure comprising at least one layer of a high barrier PCTFE film which may be used in the construction of a multi-layer film

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structure which optionally may be permanently deformed to form an article.

In a yet further aspect of the present invention, there is provided a film structure comprising at least
5 one layer of a high barrier PCTFE film which may be laminated with at least one further film of a dissimilar composition, wherein the structure is a multilayered thermoformed article which is especially useful as a packaging container for medicaments or
10 pharmaceutical compositions.

These and yet further aspects of the present invention will become more apparent with reference to the following description of the present invention.

15 DESCRIPTION OF INVENTION AND THE PREFERRED EMBODIMENTS

The present invention provides a poly(chlorotrifluoroethylene) PCTFE film with improved water vapor barrier properties over other PCTFE films known to the art. The PCTFE film taught herein may be
20 a single film structure or in the alternative, the PCTFE film as taught in the present invention may be utilized in forming a multi-layer film structure wherein the PCTFE film comprises at least a single layer of a multi layer film. Such films as taught
25 herein may be utilized in the formation of articles which include the films according to the present invention. Contemplated among these articles include bags, sheeting used for wrapping articles, or thermoformed containers such as receptacles for foodstuffs,
30 medicaments, pharmaceutical compositions, as well as other compositions and materials.

In accordance with the present invention, there are provided multi-layer film constructions which comprise at least one film layer formed from a PCTFE
35 film forming resin wherein said film forming resin

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exhibits prior to its formation as a film a number average molecular weight " M_n " of less than about 1,000,000, preferably and less than or equal to about 800,000 and which PCTFE film formed therefrom exhibits improved barrier properties. A PCTFE film forming resins having a number average molecular weight of about 750,000 or less is most particularly preferred. The number average molecular weight of the PCTFE film forming resin may be determined in accordance with conventional techniques, for example by determining the intrinsic viscosity, " η " of a sample of the PCTFE resin in a solvent such as 2,5-dichlorobenzotrifluoride wherein the intrinsic viscosity of the sample may be correlated to the M_n by the relationship:

$$[\eta] = 6.15 \times 10^{-5} (M_n)^{0.74}.$$

Such a method is more fully described in *Encyclopedia of Polymer Science and Engineering*, (c) 1985, Volume 3, published by John Wiley & Sons, at page 476.

The film forming resins used to form the multi-layer film constructions provided by the present invention may also be alternately be characterized in accordance with the specifications outlined in ASTM-D 1430-81 which provides the "zero strength time" or interchangeably referred to as the "ZST" of the film. Briefly, ASTM-D 1430-81 utilizes a compression molded test sample formed of the PCTFE resin having dimensions of about 1.6mm by 4.8 mm by 50 mm, and which has dual "v" shaped notches in the center; the sample is suspended from one end with a 7.5 g weight suspended to the other, lower end in an oven at 250°C. The ZST value is the time in seconds after which the sample breaks. The ZST value is known to reasonably correlate to the molecular weight of the resin used to form the test sample. In the practice of the present invention, the PCTFE film forming resin exhibits prior to its

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formation as a film said PCTFE film forming exhibits a zero strength time of less than about 200, preferably less than or equal to or about 180, and most preferably less than or equal to about 150.

5 The PCTFE film forming film to be ultimately used in the multi-layer films are formed from a PCTFE film forming having the qualities described immediately above. Conventional methods may be utilized or modified to produce a suitable film forming resin. Such
10 processes include bulk polymerization via the utilization of one or more peroxides as an initiating system; aqueous suspension polymerization with redox-initiator systems which include one or more alkali metal persulfates as an oxidant, one or more alkali
15 metal bisulfites as activators, and metal salts as accelerators; emulsion polymerization utilizing fluorocarbon and chlorofluorocarbon emulsifiers are also known. The molecular weight of the PCTFE film forming resin produced may be controlled by variance of
20 the reactor temperature and pressure, as well as the reaction time in order to produce suitable PCTFE film forming resin.

By way of example, one suitable process, a reduction-oxidation type reaction, comprises the steps
25 of charging a sufficient quantity of the starting reactant PCTFE to a glass lined, jacketed, stirred sealable reactor which is capable of operating at least to pressures of about 200 psig. It is preferred that the reactor include a cooling jacket or other cooling
30 means which is capable to withdraw heat from the reactor during the production process and thereby provide a means of temperature control during the reaction of the contents of the reactor.

The reaction system requires the use of an
35 initiator/catalyst system to produce the PCTFE film

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forming resin from chlortrifluoroethylene monomer. Such an initiator/catalyst system comprises reduction, oxidation and acceleration constituents wherein the oxidation constituents provide free radicals for the initiation of the polymerization of the CTFE. By way of example, suitable reduction constituents include one or more chemicals selected from the group which includes; an alkali metal bisulfate and alkali metal persulfate. Suitable oxidation constituents include one or more chemicals selected from the group which includes: hydrogen peroxide, and various metallic persulfates, including sodium persulfate and potassium persulfate, as well as ammonium persulfite. Suitable acceleration constituents include one or more chemicals selected from the group which includes: variable valence metal salts such as ferrous sulphate, silver nitrate as well as copper sulfate. Varying ratios of these constituents may be used; i.e. the ratio of the oxidation to the reduction constituents may be varied from 1:1 to 3:1, and the activator may be included in amounts to comprise to 1000 parts per million ("ppm") as well as greater amounts.

Other processes and systems suitable for the production of PCTFE film forming and copolymer resins are described in U.S. Patent Nos. 2,705,706; 2,700,622; 2,689,241; 2,569,524; 2,783,219; 2,820,026; 3,640,985; 3,671,510; 3,642,754; 3,632,847; 3,014,01. The control of the reaction conditions leads to the production of PCTFE film forming resins which are within the specified range of suitable ZST values.

It is contemplated that the PCTFE film forming resin may include minor amounts, i.e. generally up to 1% by weight of an ethylene compound containing fluoride, including: fluorinated α -olefins, such as hexafluoropropylene, hexafluoroisobutylene, vinylidene

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fluoride, tetrafluoroethylene, chlorotrifluoroethylene; fluorinated ethers such as perfluoroalkyl vinyl ethers such as perfluoropropyl vinyl ether; perfluoroalkyl ethylenes such as perfluorobutyl ethylene, and the like.

The PCTFE film forming compositions which are readily processable are formed into films in accordance with any conventionally known technique. By way of illustration and by way of limitation these include the extrusion of the film-forming composition through a flat die to form a flat cast film, or extruding the film through a circular die and inflating the annulus of the film formed thereby to form a blown film, or by casting or otherwise forming a billet from the film forming composition and thereafter skiving the billet to form a film, as well as other methods. Of these, the production of the film by means of a flat die and subsequent casting are to be generally preferred. In accordance with this method, the post extrusion conditions of the film-forming composition may be more adequately controlled in accordance with the process being taught herein. Nonetheless, it is to be understood the alternate methods may also be utilized in accordance with the process being taught herein.

In accordance with the preferred embodiment, the film forming composition is provided to an extruder whereupon the PCTFE film forming is plastificated by the action of heat and mechanical motions supplied by the extruder and extruder screw. The plastificated film forming composition is then forced through the film-forming slit of a flat die to form a film, typically having a thickness of between about 0.01 and 15 mils thick, and preferably and most preferably between about 0.1 and 10 mils thick. Thereafter, the extruded film-forming composition is contacted with a

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casting roll whereupon the film is quickly cooled, quenching the crystallization of the PCTFE.

In accordance with the present invention, the process of forming films from the PCTFE film-forming composition includes the necessary process step of rapidly cooling the extruded film. Whereas in conventional film forming operations, a conventional casting roll temperature is typically in the range of between about 250°C and 290°C, it has been surprisingly found by the present inventors that when the temperature of the casting roll is within the range of between about 150°C and 210°C, and maintained at a temperature within this range, the casting roll temperature assures that the rapid quenching of the PCTFE film which exits the extruder at a temperature of between about 500°C and 600°C occurs due to the sudden change in temperature drop.

The inventors have also realized in the present invention that the use of a PCTFE comprising film having the range of number average molecular weights or the zero strength time values outlined above provides a PCTFE film forming composition which is readily processable in accordance with conventional film forming methods to produce a film comprising essentially no additional comonomers or other constituents which reduce the ultimate barrier characteristics of the PCTFE comprising film.

The inventors of the present invention have also realized that the film formed from the PCTFE film forming compositions described above exhibits excellent barrier characteristics, particularly barrier to water vapor. Films according to the present invention exhibit a water vapor transmission rate of up to 0.03 grams of water/100 square inches over 24 hours at 100°F and 100% relative humidity for a 1 mil thickness;

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preferable the films according to the invention exhibit a water vapor transmission rate of up to about 0.025 grams of water/100 square inches over 24 hours at 100°F and 100% relative humidity for a 1 mil thickness; most
5 preferable the films according to the invention exhibit a water vapor transmission rate of up to about 0.020 grams of water/100 square inches over 24 hours at 100°F and 100% relative humidity for a 1 mil thickness.

While not wishing to be bound by any theory, it is
10 believed that such improved barrier properties are a consequence of the absence of large amounts of additional comonomers, particularly the absence of conventional comonomers in excess of amounts of 1% by weight of a PCTFE film forming resin which are used in
15 conjunction with PCTFE polymers, particularly vinylidene fluoride and/or tetrafluoroethylene which reduce the barrier properties of a PCTFE film, and further, due to the highly crystalline nature of the PCTFE film formed from the PCTFE described above in
20 accordance with the process steps outlined above. The inventors have attained excellent results with the preferred compositions according to the present invention, wherein the film forming resin composition consists essentially of a homopolymer resin of PCTFE
25 and no additional comonomers.

The formation of the films from the PCTFE composition taught by the present invention by means of a conventional film casting techniques are generally to be preferred as such production methods allow for the
30 formation of films which are ultimately useful for forming one layer of a multi-layered film structure. As will be realized by those skilled in the art, films herein having improved water vapor barrier properties may be combined with one or more other films featuring
35 of the desirable characteristics, i.e., physical

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strength, thermo-formability, color, appearance, in forming an article.

Exemplary films which may be used in conjunction with the PCTFE films of the present invention to form
5 multi-layer film structures or alternately known to the art as film laminates include one or more of the following films or film forming compositions:
acrylonitrile butadiene-styrene,
rubber modified acrylonitrile methyl acrylate
10 copolymer,
cellulostic films including cellulose acetate,
cellulose triacetate,
cellulose acetate butyrate,
cellulose propionate,
15 ethyl cellulose,
cellophane,
fluoroplastic films including
ethylenetrifluoroethylene copolymer (ETFE),
ethylenetetrafluoroethylene copolymer (ETFE),
20 fluorinated ethylene-propylene copolymer (FEP),
perfluoroalkoxy (PFA),
polychlorotrifluoroethylene copolymers (PCTFE),
polytetrafluoroethylene (PTFE),
polyvinylfluoride (PVF),
25 polyvinylidene fluoride (PVDF),
ionomer films,
polyamide films including unoriented, monoaxially oriented, or biaxially films, including films including
nylon 6, nylon 12 as well as polyamide copolymers and
30 blends of each of the above,
polybutylene,
polycarbonate (PC),
polyalkylene terephthalate, including,
polybutylene terephthalate (PBT),

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polyethylene terephthalate (PET), as well as films comprising polyester copolymer, particularly those copolymers comprising polyethylene terephthalate with at least one additional comonomer, including
5 but not limited to those known to the art as "PET-G" films and commercially marketed under the name KODAR® by the Eastman Kodak Co.,
polyethylene and polyethylene copolymer films including low density polyethylene (LDPE),
10 medium density polyethylene (MDPE),
high density polyethylene (HDPE),
ultrahigh molecular weight polyethylene (UHMWPE),
ethylene-vinyl acetate copolymers (EVA),
polyimide films,
15 polymethylmethacrylate films, (both "standard" and "type A")
polymethylpentene,
polypropylene (PP) films including cast, unoriented, monoaxially oriented, or biaxially oriented,
20 polystyrene,
polyurethane,
polyvinyl chloride (PVC),
sulfone polymer films,
vinyl chloride-acetate copolymer,
25 vinylidene chloride-vinyl chloride films,
vinyl nitrile rubber alloy films, as well as others not particularly noted here.

The PCTFE comprising films of the present invention are to be combined with such other films in
30 accordance with conventional methods, including coextrusion of the films to form a laminar film structure, or by lamination of the films into a laminar film structure, with or without the use of a composition which acts to form a "tie layer" between
35 the PCTFE comprising film and the other film or films

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used to form the laminar film structure. Such compositions which act as "tie layers" may be any of those conventionally known and used, as well as other materials which provide adhesion of the PCTFE comprising film with at least one other film to form a laminar film structure. Of these methods, lamination of the polytrichloroethylene films is preferred, as such offers the widest range of laminar film structures.

- 10 In one embodiment, the PCTFE comprising film taught herein may be incorporated into a multi-layered film structure such as may be achieved by the lamination of the PCTFE comprising film with one or more thermoplastic films which are thermoformable.
- 15 Particularly, polyvinyl chloride and polyethylene terephthalate films and copolyesters comprising polyethylene terephthalate may be mentioned here. The beneficial feature of the two or more films may be optimized to provide a suitable packaging container.
- 20 By way of example, a PCTFE comprising film may contribute excellent vapor barrier characteristics and when combined with a PVC film or alternatively a polyethylene terephthalate film which provides good physical strength characteristics, a packaging
- 25 structure providing the benefits of both such the films, good water vapor transmission barrier properties and good physical strength, may be produced. Further, in such a packaging container, the PCTFE comprising film may be oriented to contain and contact the
- 30 material, such as a foodstuff or medicament, while the PVC or polyethylene terephthalate may form the outer layer of the laminated and thermoformed film structure.

The PCTFE films may be laminated to other
35 polymeric films in accordance with any suitable

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technique which includes the conventionally known techniques of extrusion lamination wherein the two or more films are coextruded and the extruded films are combined to form a multi-layer film structure; by
5 adhesive lamination where two or more films which have been formed by any technique are provided with an intermediate layer of an adhesive material or constituent which forms a "tie layer" to thereby produce the multilayer film.

10 The films, whether comprising a single layer of the PCTFE comprising film forming composition or a multi-layer film, may optionally be stretched or oriented in any direction if so desired. In such a stretching operation, the film may be stretched in
15 either the direction coincident with the direction of movement of the film being withdrawn from the casting roll, also referred to in the art as the "machine direction", or in a direction which is perpendicular to the machine direction, and referred to in the art as
20 the "transverse direction", or in both the machine direction and the transverse direction. It is to be understood that in embodiments where the PCTFE comprising film taught herein is to be used in a multilayer film structure, that less than all of the
25 films within a multilayer structure which are used to produce such a structure may be oriented, such as might be accomplished by the lamination of an oriented PCTFE comprising film to an unoriented PVC film by the use of an intermediate tie layer, as well as the reverse case,
30 wherein an unoriented PCTFE comprising film is laminated to an oriented PVC film. Further, it is to be appreciated that films may be subjected to orientation resulting from a stamping or molding process wherein the film is heated and deformed into a

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three dimensional structure; the regions of the film which are deformed undergo orientation.

The multi-layer films formed by any of the above methods may ultimately be of any thickness desired and includes those which have thicknesses less than 100 mils. As is known to the art, a "mil" is a common unit equivalent to 0.001 inch and is typically used to describe film thicknesses. Preferably, the films have a thickness in the range of about 0.01 mil and about 10 mils; most preferably the films have a thickness of between about 0.01 mils and 1.0 mils. While such thicknesses are preferred as providing a readily flexible film, it is to be understood that other film thicknesses may be produced to satisfy a particular need and yet fall within the present invention's scope; such thicknesses which are contemplated include plates, thick films, and sheets which are not readily flexible at room temperature (approx. 20 deg.C).

The films taught in the present invention are particularly useful for forming packaging or containers structures which require low water vapor transmission properties. These may be cast articles or thermo-formed articles such as those which may be formed from a film or sheet of the film-forming composition which is "stamped" by hot die, by a "vacuum drawing", a technique also known as "embossing" wherein a film or sheet of the film-forming composition is deformed by the use of a vacuum, (and optionally may be also simultaneously mechanically deformed) thereby effectively deforming the film into a three-dimensional shape. In a preferred method, the film or sheet comprising the PCTFE film is formed by pressure forming the film by the use of a heated die wherein the film is contacted with a heated die and under the influence of heat and pressure, deformed to form a

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three-dimensional shape. An alternative packaging structure within which the present film-forming composition may be used are pouches or bags which may be formed from two pieces or sheets of films which are joined to one another so to form a containment space between the two sheets or films suitable for the containment of solids, liquids and/or gases. The film-forming compositions may also be used to form a storage vessels or containment vessels, therefrom i.e., jars, bottles, and the like which may be sealable, wherein the film-forming composition taught by the instant specification may form at least one layer of the said structure.

One particularly useful article are packaging materials associated with medicaments and pharmaceutical compositions which are provided in either a pill, capelet or capsule form. Such a packaging structure is known to the art as a "blister" pack. Blister packs conventionally comprise at least two elements, a first sheet of a thermo-formed multi-layer film which has been stamped with at least one, but more generally a plurality of indentations which form "receptacles". Such indentations extend out of the plane of the film (which may be generally be considered to be two-dimensional) to form a three-dimensional shape. Such shapes form individual receptacles are suited for the retention of a pill, capsule, or capelet. A further, second sealant sheet is generally layered in register with the film sheet which seals the individual receptacles formed within the first sheet and containing the pharmaceutical composition. Typically, the second sealant sheet is a metallic sheet such as aluminum foil or metallized film which provides good strength and low water vapor transmission and/or odor permeability. Further, a use

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of a metal or metallized sheet as the sealant sheet may be desirable as such materials being substantially opaque provide a backing with the first sheet containing the indentations and a rapid means of visual inspection by which it may be readily determined which of the contents of the receptacles have been removed from the said packaging structure. In an alternative, such a second sealant sheet may be a sheet comprised of a fibrous material such as a paper product, or of a polymeric film or sheet which may or may not be colored or which alternately may or may not be opaque.

The contents of the receptacles which are retained within a receptacle of a multi-layer film sheet and a sealant sheet may be removed by forcing the contents through the sealant sheet so to burst the sealant sheet and allow the removal of the contents, or the sealant sheet may be at least partially peeled so to separate the multi-layer film sheet from the sealant sheet and allow access to the contents.

The films of the present invention may be imparted with a conventional coloring agent or a dye or pigment so to impart a color to the laminated film structures, or alternately to render the film structures substantially opaque. Any conventional coloring agent or a dye or pigment which is appropriate for use in the films may be used. It may be desirable in particular aspects to provide a coloring agent to one of the films forming the laminated film structure, by way of example to the PVC, PET or polyethylene copolymer film with a coloring agent, which may be selected to act as a filter to block the transmission of particular radiowave frequencies, particularly those within the visible, ultraviolet and infrared spectrum bands which if transmitted to the material such as a pharmaceutical composition, medicament or foodstuff contained within a

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structure formed from the laminated film structures taught within would act to degrade the said material.

In addition to the blister pack sheet which is used to provide a structure for the packaging and retention of medicaments and pharmaceutical compositions, it is also to be understood that such a blister pack provided by the present invention may be used for the containment of other edible compositions, such as foodstuffs (including liquids or gelatinous materials), as well as compositions or articles which are not normally edible. Examples of such materials include, but are not limited to any article or composition which may be beneficially stored in a structure as taught herein, such as paints, dyes, inks, liquid slurries, aqueous slurries, or any article of manufacture which may comprise one or more of such materials. Further it should be recognized that the multi-layer film may be thermoformed into a container, such as a glass, cup, bowl, dish, or other vessel suitable for the containment of an edible or imbibable composition, i.e., foodstuffs, medicaments, pharmaceutical compositions or alternately, an inedible composition, i.e. articles of manufacture, liquids, slurries, gelatinous compositions, such as are presently known as a "single use container". In one such embodiment of such constructions, it is contemplated that a film dissimilar to the PCTFE comprising film taught herein would be in contact with the edible or imbibable composition, while the PCTFE comprising film would be used as a further layer of the thermoformed article. For example, one such article may be formed from a multilayer film comprising a polyethylene terephthalate film layered in register with the PCTFE comprising film of the present invention wherein the multilayer film is deformed to form an

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article such as a small cup so that the interior of the cup which is to ultimately contact the foodstuff to be retained in the cup contacts the polyethylene terephthalate film. In an alternative embodiment, the PCTFE comprising film of the present invention used in forming a multilayer film may also be used to form an article such that the PCTFE comprising film will ultimately contact the foodstuff, or pharmaceutical composition or medicament which is placed in the said cup.

The determination of the physical characteristics of the films may be determined using any commonly known testing procedure, including the protocols defined by the American Society of Testing Materials, including but not limited to those designated under the protocols of ASTM D 882-83 "Standard Testing Methods for Tensile Properties of Thin Plastic Sheeting". Preferably, the samples are evaluated in both the machine direction and the transverse directions. In accordance with the protocol of the ASTM D 882-83 tests, the tensile modulus is reported in units of pounds per square inch, "psi", the tensile yield strength is reported in units of psi, the yield elongation is reported in units of percent "%", the ultimate tensile strength is reported in units of psi, and the ultimate tensile elongation is reported in units of % and the Elemendorf Tear Strength is reported in terms of grams. The direction of the test measurement was relative to the direction of the film with "MD" indicative of machine direction orientation, and "TD" indicative of transverse directions orientation. The barrier characteristics of the film samples were run on sample sheets of 100 square inches at 100°F and 100% relative humidity on a Mocon Permatran Model W600 testing device in order to determine the amount of water which permeated the film;

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units for this value are (grams of water \times mil of film thickness/100 inch²/day).

The invention is more easily understood by reference to specific embodiments which are
5 representative examples according to the teachings of the instant invention. It must be understood however, that the specific embodiments discussed herein are provided only for the purpose of illustration, and not
10 understood that the invention may be practiced otherwise than specifically described and yet be within the inventive scope.

EXAMPLES

15 Film samples were produced of PCTFE films in accordance with the description described herein, as well as plural films which were produced from PCTFE copolymers, including those which comprised minor amounts of either vinylidene fluoride or
20 tetrafluoroethylene which are known to the art. The films were tested for their water vapor transmission rates, "WVTR" on the Mocon Permatran Model W600 tester and their physical characteristics in accordance with the testing protocols of ASTM D 882-83.
25 The films were produced in accordance with the following general processing conditions: the (or copolymer in the case of the comparative examples) was provided to the feed inlet of a 3 1/2 inch extruder with a general purpose mixing screw having a length to
30 diameter ratio, "L/D" of 24/1. The feed inlet was about 560°F, and the extruder was maintained at a temperature of approximately 550°F across the length of the barrel. The pressure in the extruder was about 4000 psi. The extruder was operated to produce
35 approximately 80 lbs/hours of the composition; the

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screw rotational speed was approximately 18 rpm. The extrudate exiting the extruder was then forced into a conventional film forming die head of the "coathanger" type, which had a die gap of 0.035 inches (35 mils), and a width of about 40 inches. The die head was maintained at a temperature of 620°F; the rate of film production or "line speed" was approximately 65 feet/min. The extruded film was contacted with a casting roll whose temperature was maintained at approx. 150°F, or as is noted in some instances at about 270°F. A film having a final width of about 40 inches, and a thickness of approximately 0.5 mil was produced therefrom. The particular film compositions are shown on Table 1, amounts of tetrafluoroethylene ("TFE") and/or vinylidene fluoride ("VF2") which were used as comonomers are listed with their respective weight percentages of each for respective film forming compositions, as well as the ZST values for each composition. Barrier characteristics of these film compositions are shown on Table 2, and physical properties of the film compositions are shown on Table 3.

TABLE I

Example:	C1	C2	C3	C4	C5	C6	1	2	3	4	5	6
PClE, wt. %:	97.8-98.1	97.8-98.1	97.8-98.1	97.8-98.1	96-96.8	96-96.8	100	100	100	100	100	100
TFE, wt. %:	0.9-1.2	0.9-1.2	0.9-1.2	0.9-1.2	---	---	---	---	---	---	---	---
VF ₂ , wt. %:	1	1	1	1	3.2-4.0	3.2-4.0	---	---	---	---	---	---
ZnI:	125	125	125	125	125	125	130	130	135	135	135	135

TABLE 2

Example:	C1	C2	C3	C4	C5	C6	1	2	3	4	5	6
Casting roll Temp. (deg.F):	150	190	230	270	150	270	150	270	150	150	150	150
WVTR (0.5 mil film) +-:												
Sample 1:	0.0405	0.0495	0.0402	0.0623	0.195	0.03	0.0384	0.0361	0.0299	0.0271	0.0271	0.0304
Sample 2:	0.0399	0.0447	0.0402	0.0405	0.071	0.0335	0.0379	0.0335	0.0279	0.0288	0.035	0.0283
WVTR (1.0 mil film) +-:												
Sample 1:	0.0215	0.0262	0.0237	0.0336	0.0917	0.0189	0.018	0.0166	0.019	0.017	0.021	0.019
Sample 2:	0.0231	0.0308	0.0209	0.023	0.0341	0.0211	0.0197	0.0171	0.018	0.018	0.018	0.017

WVTR determined as grams of water/100 sq.in./24 hrs at 100 deg.F and 100% RH

TABLE 3

Example:	C1	C2	C3	C4	C5	C6	1	2	3	4	5	6
Tensile Str. (psi):												
- at yield [MD]:	6530	6410	6860	7510	5820	7890	6330	8000	6356	6379	6491	6367
- at yield [TD]:	5880	5600	6790	7360	4730	7700	5870	7450	5907	5973	6035	6038
- at break [MD]:	14650	14810	16020	13440	12260	12510	14490	12290	16511	17060	15955	15762
- at break [TD]:	7150	6550	7500	6280	6810	5660	6990	6790	6693	7007	7105	6660
Elongation (%):												
- [MD]:	112	111	121	112	92	115	112	95	99	95	93	86
- [TD]:	226	225	250	232	22	242	229	263	222	233	237	219
Tensile Modulus (psi):												
- [MD]:	176100	198800	212800	235200	162800	245600	198500	245200	201966	201645	192522	208128
- [TD]:	175300	175700	193600	216100	148200	214400	169600	216100	189803	181646	181510	200287
Elmendorf Tear Strength (g/layer):												
- [MD]:	43	7	10	10	162	115	20	8	---	---	---	---
- [TD]:	53	47	66	145	27	242	49	301	---	---	---	---
Graves Tear Strength (g/mil):												
- [MD]:	---	---	---	---	---	---	---	---	353	361	394	392
- [TD]:	---	---	---	---	---	---	---	---	278	266	284	301
WVTR	0.0405	0.0495	0.0402	0.0623	0.195	0.03	0.0384	0.0361	0.0289	0.028	0.0276	0.0294

WVTR determined as grams of water/100 sq.in./24 hrs at 100 deg.F and 100% RH

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As may be seen from Table 1, the film compositions of the comparative examples C1 through C6 included amounts of comonomers in the composition of the film forming resin. The film compositions according to examples 1 - 6 consisted of a homopolymer resin comprising no additional comonomers as are included in the compositions of the comparative examples C1-C6.

The films formed in Examples C1-C6, 1-2 had a film thickness of 0.5 mil and films 3-6 had a film thickness of 0.6 mil; values on Table 2 for 1 mil thick films are normalized for that thickness from the values for the 0.5 mil film samples. All of the films were tested using the Mocon Permatran Model W600 testing device at 100°F for WVTR values.

The results of the physical testing of the film as summarized on Table 3 show improvements of the inventive compositions over films of the prior art; the films of Examples 1-6 illustrate increased barrier to water resistance in films comprising no comonomers while simultaneously preserving good physical properties. The inventors had also found that the films of C1-C4 exhibited very poor thermoformability as opposed to the films of 1-6 which were readily thermoformable.

It will be appreciated that the instant specifications and examples set forth herein are by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention, whose limitations are bounded only by the appendant claims.

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CLAIMS

1. A film formed from a poly(chlorotrifluoroethylene) comprising film forming resin is a poly(chlorotrifluoroethylene) homopolymer resin
5 containing no additional comonomers and having a ZST of 200 or less.
2. A film according to claim 1 wherein the film exhibits a water vapor transmission rate of up to 0.03
10 grams of water/100 square inches over 24 hours at 100°F and 100% relative humidity for a 1 mil thickness.
3. The film according to claim 1 further comprising a coloring agent.
15
4. The film according to any of claims 1-3 which is stretch oriented in the machine direction or in the transverse direction, or in both the machine direction and the transverse direction.
20
5. A multilayer film structure comprising at least one film layer of the film according to any of claims 1 through 4.
- 25 6. A multilayer film structure according to claim 5 which further comprises at least one second film selected from the group which consists of:
acrylonitrile butadiene-styrene film,
rubber modified acrylonitrile methyl acrylate copolymer
30 film,
cellulostic films including cellulose acetate film,
cellulose triacetate film,
cellulose acetate butyrate film,
cellulose propionate film,
35 ethyl cellulose film,
cellophane film,
fluoroplastic film,
ethylenechlorotrifluoroethylene copolymer (ECTFE) film,

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- ethylenetetrafluoroethylene copolymer (ETFE) film,
- fluorinated ethylene-propylene copolymer (FEP) film,
- perfluoroalkoxy (PFA) film,
- polychlorotrifluoroethylene copolymer (PCTFE) film,
- 5 polytetrafluoroethylene (PTFE) film,
- polyvinylfluoride (PVF) film,
- polyvinylidene fluoride (PVDF) film,
- ionomer film,
- polyamide film,
- 10 polyamide copolymer film,
- polyamide blend film,
- polybutylene film,
- polycarbonate (PC) film,
- polyalkylene terephthalate film,
- 15 polybutylene terephthalate (PBT) film,
- polyethylene terephthalate (PET) film,
- polyethylene terephthalate copolymer film,
- polyethylene film,
- polyethylene copolymer film,
- 20 low density polyethylene (LDPE) film,
- medium density polyethylene (MDPE) film,
- high density polyethylene (HDPE) film,
- ultrahigh molecular weight polyethylene (UHMWPE) film,
- ethylene-vinyl acetate copolymers (EVA) film,
- 25 polyimide film,
- polymethylmethacrylate film,
- polymethylpentene film,
- polypropylene (PP) film,
- polystyrene film,
- 30 polyurethane film,
- polyvinyl chloride (PVC) film,
- sulfone polymer film,
- vinyl chloride-acetate copolymer film,
- vinylidene chloride-vinyl chloride film, or
- 35 vinyl nitrile rubber alloy film.

7. A multilayer film according to claim 5 or 6 wherein either the poly(chlorotrifluoroethylene) film or the second film contains a coloring agent.

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8. A multilayer film according to any of claims 5 through 7 which further comprises a tie layer intermediate the poly(chlorotrifluoroethylene) film and the second film.

5

9. An article produced using the film according to any preceeding claim wherein the article is produced using a thermoforming step.

INTERNATIONAL SEARCH REPORT

PCT/US 92/08064

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08J5/18; B32B27/08

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	C08J ; C08F ; B32B

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB,A,807 432 (W.T. MILLER) 14 January 1959	1,2
Y	see column 1, line 33 - line 40; claims ---	4-6,8
Y	EP,A,0 136 922 (E.I. DU PONT DE NEMOURS AND COMPANY) 10 April 1985 see the whole document ----	4-6,8
X	PATENT ABSTRACTS OF JAPAN 20 November 1985 & JP,A,60 135 446 (OTSUKA KAGAKU YAKUHIN KK) 18 July 1985 see abstract -----	1,3,9
A	US,A,3 024 224 (R.L. HERBST ET AL) 6 March 1962 ----- -/-	1

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Date of the Actual Completion of the International Search

25 NOVEMBER 1992

Date of Mailing of this International Search Report

- 4. 12. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

DE JONGE S.J.P.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	DATABASE WPIL Week 2890, Derwent Publications Ltd., London, GB; AN 90-212373 & JP,A,2 141 224 (SHINETSU CHEM IND KK) 30 May 1990 see abstract ---	1,2,4-6, 8
A	PATENT ABSTRACTS OF JAPAN 29 November 1988 & JP,A,63 179 950 (NITTO ELECTRIC IND CO LTD) 23 July 1988 see abstract ---	1
A	EP,A,0 132 583 (ALLIED CORPORATION) 13 February 1985 see claims 1-3 -----	1,5,6

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

**US 9208064
SA 65228**

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The members are as contained in the European Patent Office EDP file on
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EP-A-0136922	10-04-85	US-A- 4544721	01-10-85
		AU-A- 3362884	18-04-85
		CA-A- 1228964	10-11-87
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		JP-C- 1575639	24-08-90
		JP-B- 2001654	12-01-90
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		DE-A- 3474006	20-10-88
		JP-A- 60054832	29-03-85
		US-A- 4677017	30-06-87

EP0 FORM P0679

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